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Heisei 6-73397 (1994)

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(54) [Title of the Invention]

Novel Photoactivating Agent, Novel Bleaching Agent, Novel Disinfecting agent

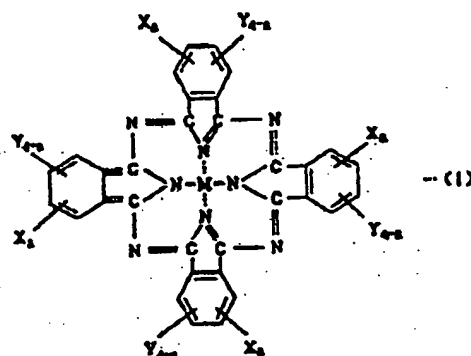
(57) [Summary]

[The Purpose] This invention describes photoactivating agents, particularly bleaching or disinfecting agents, which contain certain phthalocyanine compounds as active elements, that are effective for bleaching fabrics, removing stains, and controlling bacteria inside or on substrates.

[Constitution] Photoactivating agents, bleaching agents, or disinfecting agents which contain phthalocyanine compounds that are shown in general formula (I).

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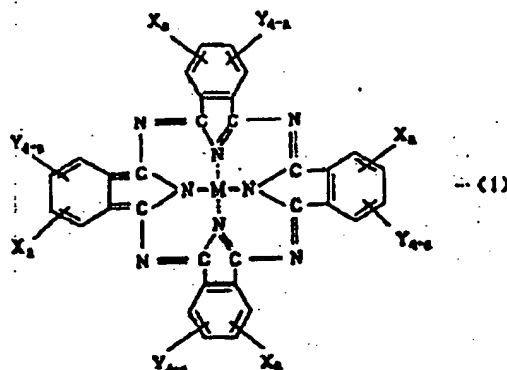
[Chem 1]



[Scope of Patent Claim]

[Claim 1] Photoactivating agents which contain phthalocyanine compounds that are indicated in the following general formula (I).

[Chem 1]



[In this formula, each X variable independently stands for H, F, OR₁Zb-e, SR₂Zf-i, OR₃, and SR₄, respectively. (However, R₁ and R₂ individually stand for a phenyl or a benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxycarbonyl group, or halogen. R₃ and R₄ individually stand for a C₁-C₂₀ alkyl group and a C₄-C₆ cycloalkyl group, and, Z stands for a sulfonyl group.) Each Y variable independently stands for OR₅Zj-m, SR₆Zn-q. (R₅ and R₆ individually stand for a phenyl group or a benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxycarbonyl group, or halogen. Z stands for a sulfonyl group.) The variable a is an integer between 0 and 3, variables b-q are integers between 0 and 7, and the sum of variables b through q is 1 or greater. M stands for zinc, aluminum chloride, or gallium chloride.]

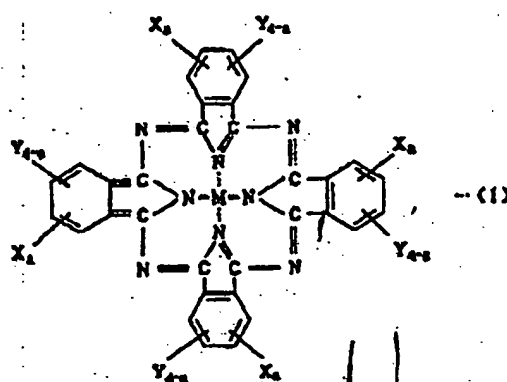


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[Claim 2] Bleaching agents which contain phthalocyanine compounds that are indicated in the following general formula (I).

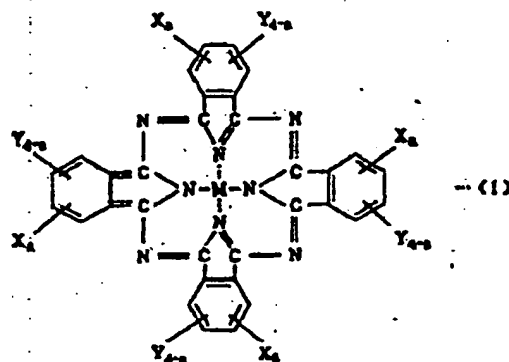
[Chem 2]



[In this equation, each X variable independently stands for H, F, OR₁Zb-e, SR₂Zf-i, OR₃, and SR₄, respectively. (However, R₁ and R₂ individually stand for a phenyl or benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxycarbonyl group, or halogen. R₃ and R₄ individually stand for a C₁-C₂₀ alkyl group and a C₆-C₈ cycloalkyl group, and, Z stands for a sulfonyl group.) Each Y variable independently stands for OR₅Zj-m and SR₆Zn-q. (R₅ and R₆ individually stand for a phenyl group or a benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxycarbonyl group or halogen. Z stands for a sulfonyl group.) The variable a is an integer between 0 and 3, variables b-q are integers between 0 and 7, and the sum of variables b through q is 1 or greater. M stands for zinc, aluminum chloride, or gallium chloride.]

[Claim 3] Disinfecting agents which contain phthalocyanine compounds that are indicated in the following general formula (I).

[Chem 3]



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[In this equation, each X variable independently stands for H, F, OR₁Zb-e, SR₂Zf-i, OR₃, and SR₄, respectively. (However, R₁ and R₂ individually stand for a phenyl or a benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxy carbonyl group, or halogen. R₃ and R₄ individually stand for a C₁-C₂₀ alkyl group and a C₆-C₆ cycloalkyl group, and, Z stands for a sulfonyl group.) Each Y variable independently stands for OR₅Zj-m and SR₆Zn-q. (R₅ and R₆ individually stand for a phenyl group or a benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxy carbonyl group, or halogen. Z stands for a sulfonyl group.) The variable a is an integer between 0 and 3, variables b-q are integers between 0 and 7, and the sum of variables b through q is 1 or greater. M stands for zinc, aluminum chloride, or gallium chloride.]

[Detailed Explanation of the Invention]

[0001]

[Areas of Application in Industry] This invention describes photoactivating agents. More specifically, this invention describes potential photoactivating agents, which contain certain kinds of phthalocyanine elements as active components, that are effective for bleaching fabrics, removing stains, and controlling bacteria inside or on substrates.

[0002]

[Existing Technology] It has been reported that water-soluble zinc phthalocyanine compounds or aluminum phthalocyanine compounds are effective detergents or bleaching agents for fabrics. (For example, Patent No. 50-113479, Patent No. 51-4205, Patent No. 52-155279, Patent No. 53-119381, Patent No. 54-135806, Patent No. 54-145712, and Patent No. 58-150000)

[0003] It has also been shown that water-soluble zinc phthalocyanine compounds or aluminum phthalocyanine compounds are sometimes effective for controlling bacteria on substrates. (For example, Patent No. 53-119884 and Patent No. 1-279807) However, these compounds do not always show satisfactory effects and are also somewhat expensive.

[0004]

[The Issues to Be Resolved by the Invention] This invention aims to solve the problems which were stated above. The purpose of this invention is to provide more effective photoactivating agents, particularly potential compounds for use as bleaching or disinfecting agents, which possess more powerful performance than other compounds reported previously.

[0005]

[Means to Resolve the Issues of Concern] In order to solve the issues stated above, after thorough investigation, we found that certain kinds of phthalocyanine compounds can be potential photoactivating agents, particularly bleaching or disinfecting agents, which led us to establish this invention. In this invention, phthalocyanine compounds are substituted with at least an etherallyl group or thioetherallyl group, and can also possess either a fluorine group, etherallyl group, thioetherallyl group, or etherallyl group, in which the allyl substituents are sulfonated.

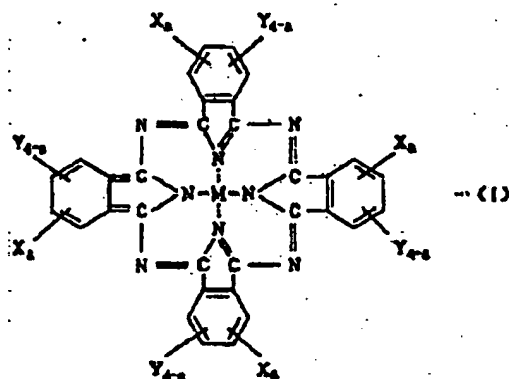
[0006]

According to this invention, the compounds which contain the novel fluorinated phthalocyanine which is shown in general formula (I) are provided as the photoactivating agents.

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[0007]
[Chem 4]

[0008] [In this equation, each X variable independently stands for H, F, OR, Zb-e, SR₂Zf-i, OR₃, and SR₄, respectively. (However, R₁ and R₂ individually stand for a phenyl or benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxycarbonyl group, or halogen. R₃ and R₄ individually stand for a C₁-C₂₀ alkyl group and a C₄-C₆ cycloalkyl group, and Z stands for a sulfonyl group.) Each Y variable independently stands for OR₅Zj-m, SR₆Zn-q. (R₅ and R₆ individually stand for a phenyl group or a benzyl group. The phenyl or benzyl group can be substituted with C₁-C₄ alkyl group, alkoxy group, carboxyl group, alkoxycarbonyl group, or halogen. Z stands for a sulfonyl group.) The variable a is an integer between 0 and 3, variables b-q are integers between 0 and 7, and the sum of variables b through q is 1 or greater. M stands for zinc, aluminum chloride, or gallium chloride.]

[0009] The examples for the compounds described above are as follows: X is substituted with a hydrogen atom, fluorine atom, methoxy group, ethoxy group, butoxy group, octyloxy group, cyclohexyloxy group, phenoxy group, carboxylphenoxy group, methoxycarbonyl phenoxy group, ethoxycarbonyl phenoxy group, benzoyloxy group, tolyloxy or xylyloxy group which can be partially sulfonated, phenoxy group which is substituted with fluorine or chlorine, methylthio group, ethylthio group, butylthio group, octylthio group, cyclohexylthio group, phenylthio group, carboxylphenylthio group, methoxycarbonyl phenylthio group, ethoxycarbonyl phenylthio group, benzylthio group, tolythio or xylythio group which can be partially sulfonated, phenylthio group which is substituted with fluorine or chlorine, phenoxy group, carboxyl phenoxy group, methoxycarbonylphenoxy group, ethoxycarbonylphenoxy group, benzoyloxy group, tolyloxy group or xylyloxy group in which Y are partially sulfonated, phenoxy group which is substituted with fluorine or chlorine, phenylthio group, carboxylphenylthio group, methoxycarbonyl phenylthio group, ethoxycarbonyl phenylthio group, tolylthio or xylythio group which are partially sulfonated, or phenylthio group which is substituted with fluorine or chlorine. The M is zinc, aluminum chloride, or gallium chloride. The compounds are also supposed to possess 1-16 sulfonyl groups per 1 mol of phthalocyanine compound.

[0010] The following lists the phthalocyanine compounds which are used in this invention and that are indicated in general formula (I) described above. The preferential phthalocyanine compounds are those which possess allyl groups that are sulfonated. Zinc, Aluminum Chloride, or Gallium Chloride are suitable for the

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central metal. In addition, one to twenty sulfonyl groups are introduced to one mole of phthalocyanine compound. However, the more suitable compounds are those in which 1-10 sulfonyl groups are introduced.

[0011]

The skeleton of type A:

4,5-octakis(phenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(PhS)8
4,5-octakis(o-methylphenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-MePhS)8
4,5-octakis(p-methylphenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(p-MePhS)8
4,5-octakis(p-fluorophenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(p-FPhS)8
4,5-octakis(o-methoxyphenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-MeOPhS)8
4,5-octakis(p-methoxyphenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(p-MeOPhS)8
4,5-octakis(o-carboxyphenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-cPhS)8
4,5-octakis(p-carboxyphenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(p-cPhS)8
4,5-octakis(phenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(PhO)8
4,5-octakis(o-methylphenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-MePhO)8
4,5-octakis(p-methylphenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(p-MePhO)8
4,5-octakis(o-methoxyphenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-MeOPhO)8
4,5-octakis(p-methoxyphenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(p-MeOPhO)8
4,5-octakis(o-fluorophenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-FPhO)8
4,5-octakis(o-carboxyphenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-cPhO)8
4,5-octakis(p-carboxyphenoxy)-3,6-octafluorophthalocyanine
abbreviation; PcF8(p-cPhO)8

The skeleton of type B:

4-tetrakis(phenoxy)-5-tetrakis(phenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(PhO)4(PhS)4
4-tetrakis(phenoxy)-5-tetrakis(o-methylphenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(PhO)4(o-MePhS)4
4-tetrakis(phenoxy)-5-tetrakis(p-fluorophenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(PhO)4(p-FPhS)4
4-tetrakis(o-methoxyphenoxy)-5-tetrakis(phenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-MeOPhO)4(o-MePhS)4
4-tetrakis(o-carboxyphenoxy)-5-tetrakis(phenylthio)-3,6-octafluorophthalocyanine
abbreviation; PcF8(o-cPhO)4(PhS)4
4-tetrakis(tetrafluorophenoxy)-5-tetrakis(phenylthio)-3,6-octafluorophthalocyanine

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abbreviation ; PcF8(F4PhO)4(PhS)4

4-tetrakis(methoxy)-5-tetrakis(phenylthio)-3,6-octafluorophthalocyanine

abbreviation ; PcF8(MeO)4(PhS)4

4-tetrakis(phenoxy)-5-tetrakis(tetrafluorophenoxy)-3,6-octafluorophthalocyanine

abbreviation ; PcF8(PhO)4(F4PhO)4

4-tetrakis(phenoxy)-5-tetrakis(methoxy)-3,6-octafluorophthalocyanine

abbreviation ; PcF8(PhO)4(MeO)4

4-tetrakis(phenoxy)-5-tetrakis(benzoyloxy)-3,6-octafluorophthalocyanine

abbreviation ; PcF8(PhO)4(BzO)4

The skeleton of type C:

4-tetrakis(phenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(PhO)4

4-tetrakis(o-methylphenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(o-MePhO)4

4-tetrakis(p-methylphenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(p-MePhO)4

4-tetrakis(o-fluorophenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(o-FPhO)4

4-tetrakis(o-methoxyphenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(o-MeOPhO)4

4-tetrakis(p-methoxyphenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(p-MeOPhO)4

4-tetrakis(o-carboxyphenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(o-cPhO)4

4-tetrakis(p-carboxyphenoxy)-3,5,6-dodecafluorophthalocyanine

abbreviation ; PcF12(p-cPhO)4

The skeleton of type D:

4-tetrakis(phenoxy)phthalocyanine

abbreviation ; Pc(PhO)4

4-tetrakis(o-methylphenoxy)phthalocyanine

abbreviation ; Pc(o-MePhO)4

4-tetrakis(p-methylphenoxy)phthalocyanine

abbreviation ; Pc(p-MePhO)4

4-tetrakis(o-fluorophenoxy)phthalocyanine

abbreviation ; Pc(o-FPhO)4

4-tetrakis(o-methoxyphenoxy)phthalocyanine

abbreviation ; Pc(o-MeOPhO)4

4-tetrakis(p-methoxyphenoxy)phthalocyanine,

abbreviation ; Pc(p-MeOPhO)4

4-tetrakis(o-carboxyphenoxy)phthalocyanine

abbreviation ; Pc(o-cPhO)4

4-tetrakis(phenylthio)phthalocyanine

abbreviation ; Pc(PhS)4

4-tetrakis(o-methylphenylthio)phthalocyanine

abbreviation ; Pc(o-MePhS)4

4-tetrakis(p-methylphenylthio)phthalocyanine

abbreviation ; Pc(p-MePhS)4

4-tetrakis(o-fluorophenylthio)phthalocyanine



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abbreviation; Pc(o-FPhS)₄
4-tetrakis(o-methoxyphenylthio)phthalocyanine
abbreviation; Pc(o-MeOPhS)₄
4-tetrakis(p-methoxyphenylthio)phthalocyanine
abbreviation; Pc(p-MeOPhS)₄
4-tetrakis(o-carboxylphenylthio)phthalocyanine
abbreviation; Pc(o-cPhS)₄
4-tetrakis(p-carboxylphenylthio)phthalocyanine
abbreviation; Pc(p-cPhS)₄

[0012] The synthetic procedures for type A-C of phthalocyanine compounds (general formula I) has already been reported by us in Patent No. 63-65806, Patent No. 1-103554, Patent No. 1-103555, Patent 1-209599, and Patent No. 4-42586. The following scheme indicates the synthetic procedures for those compounds. In addition, the synthetic procedures for type D will be described as examples.

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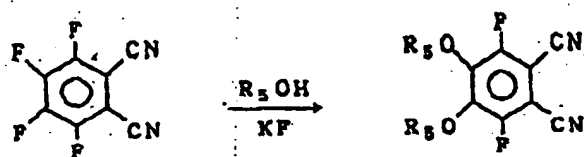
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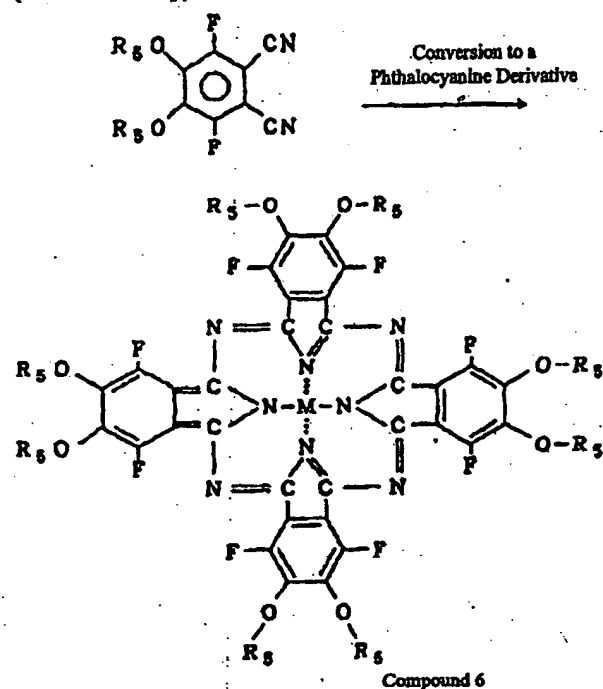
[0013]
[chem 5]

Type A Synthetic Method (1)

(The First Step)



(The Second Step)



Compound 6

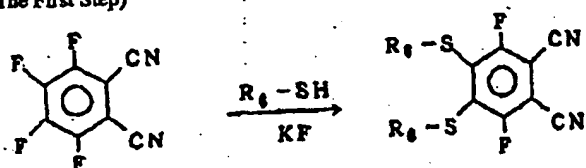
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[0014]

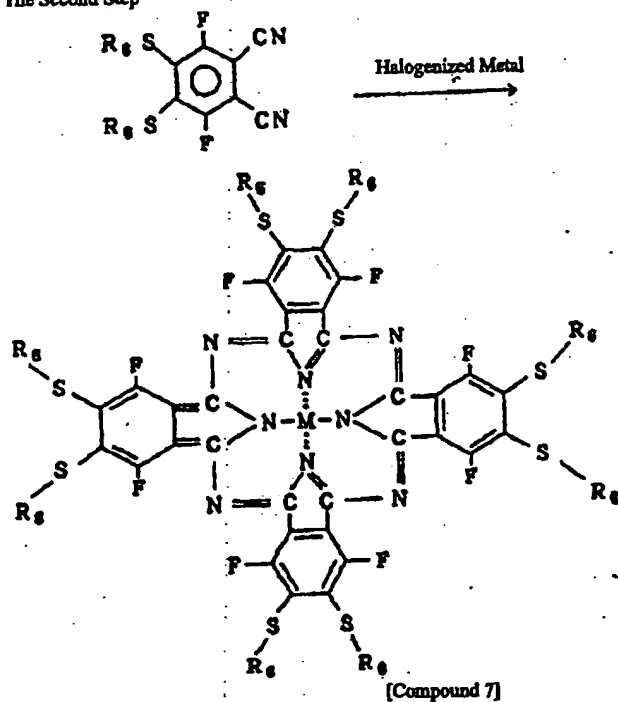
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Type A Synthetic Method (2)

(The First Step)



The Second Step



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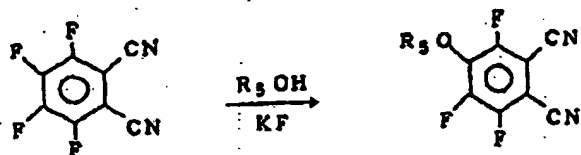
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[0015]

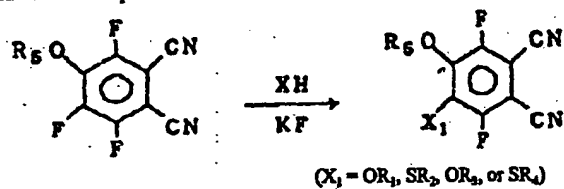
[chem 7]

Type B Synthetic Method

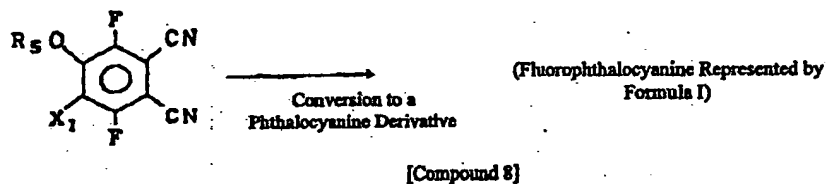
(The First Step)



The Second Step



(The Third Step)



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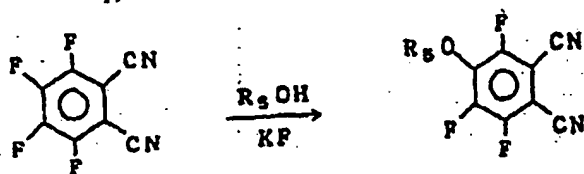
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[0016]

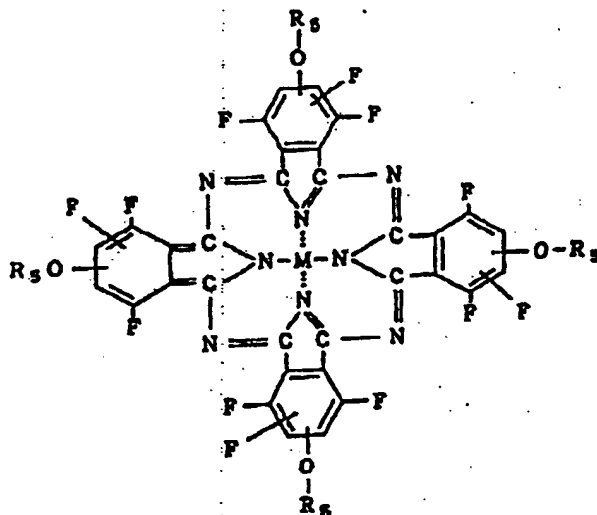
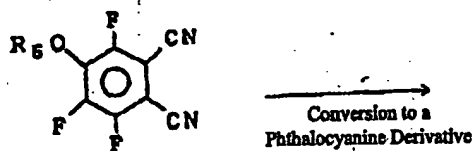
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Type C Synthetic Method

(The First Step)



(The Second Step)



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[0017] In each formula of each step in each synthetic procedure R_1, R_2, R_3, R_4, R_5 , and R_6 are the same as R_1, R_2, R_3, R_4, R_5 , and R_6 in general formula (I). In addition, in the first step of the synthetic procedure for type A, the first and the second steps of the synthetic procedure for type B, and the first step of the synthetic procedure for type C, nitrile derivatives such as acetonitrile and potassium fluoride can be used for the reaction solvent and condensing agent, respectively. The reaction condition of the first step for the synthetic procedure of type C is the same as the first step for the synthetic procedure of type A, except for the submission ratio for ROH and KF and tetrafluorophthalonitrile.

[0018] In the synthetic procedure for type B, a milder reaction condition is possible, which affords incompletely substituted compounds where fluorine partially remains at the 4 position without being substituted with OR. These incompletely substituted compounds can be utilized as the starting materials for the second reaction step. The milder reaction conditions can also apply to the second step, which will afford incompletely substituted compounds where fluorine partially remains at the 5 position without being substituted with OR or SR. These incompletely substituted compounds can also be utilized as the starting materials for the third step. The same idea can also apply to the synthetic procedures for type A and C. Namely, milder reaction conditions will afford incompletely substituted compounds where fluorines partially remain at the 4 or 5 positions without being substituted with OR or SR. These incompletely substituted compounds can also be utilized as the starting materials for the second steps. In these cases, the final phthalocyanine compound products are supposed to contain incompletely substituted phthalocyanines that partially possess fluorines at the 4 or 5 positions, in addition to those at the 3 and 6 positions. However, this contamination does not hinder the compound's performance as long as it does not affect their physical properties such as solubility.

[0019] An example for the synthesis of type D compound

The synthesis of 4-phenylthiophthalonitrile

In a 100 ml separable flask, 26.0 g (0.15 mol) of 4-nitrophthalonitrile, 16.2 g (0.15 mol) of thiophenol, and 20 ml of N, N-dimethylformamide were mixed. To this initial mixture, an additional mixture of 1,100 ml of N, N-dimethylformamide and 22.84 g (0.15 mol) of 1,8-diazabicyclo [5.4.0]undec-7-ene was added dropwise over an hour at room temperature. After the addition, the reaction mixture was warmed to 100°C and the reaction was allowed to continue for an additional three hours. After the reaction was completed, the reaction mixture was poured into 500 ml of 1% aqueous hydrochloric acid solution and the precipitated solid was washed with water and dried in vacuo to afford 30 g of the desired yellow cake. (Yield 86.4%)

[0020] The synthesis of 4-tetrakisphenylthio zinc phthalocyanine

In a 100 ml separable flask, 3.54 g (15 mol) of 4-phenylthiophthalonitrile, 1.44 g (18 mmol) of zinc iodide, and benzonitrile were distilled off to afford solid material. This solid material was washed with 200 ml of methanol twice and afforded 3.34 g of the desired green cake. (Yield 88.2%)

[0021] The synthesis of sulfonated 4-phenylthiophthalonitrile

In a 100 ml separable flask, 2.02 g (2 mmol) of 4-tetrakisphenylthio zinc phthalocyanine and 50 ml of 1,1,2,2-tetrachloroethane was stirred at 80°C. The mixture of 25 ml of 1,1,2,2-tetrachloroethane and 2.08 g (8 mmol) of chlorosulfonic acid was added dropwise to the reaction mixture over 30 minutes. After the addition, the reaction mixture was warmed to 140°C and the reaction was allowed to continue for an additional two hours. After the reaction was completed, the precipitated solid was washed twice with 200 ml of dichloromethane to afford 2.42 g of the desired green cake. After analysis, this product was found to possess four sulfonyl groups in one molecule. Furthermore, this method can also be applied to the other compounds of type D.

[0022] These phthalocyanine compounds that are described in this invention are effective photoactivating agents. They show an excellent light absorption, particularly toward 680 nm and above, and its primary and secondary effects are useful for various applications. Particularly, these effects are applicable for bleaching fabrics, removing stains from fabrics, and for disinfection. In the cases of bleaching fabrics or removing stains

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from fabrics, one can follow reported methods in the presence of oxygen, water, and under the irradiation of solar light or artificial light such as incandescent lamp.

[0023] A method for bleaching and removing stains from fabrics follows: fabrics which have stains and dirt are treated repeatedly for a certain period of time under the light described above with the detergent solution which contain the water-soluble phthalocyanine compounds described in this invention. By photoactivated phthalocyanine, this treatment generates singlet oxygen etc. which removes stains and bleaches the fabrics.

[0024] The phthalocyanine compounds in this invention can be used as disinfectants, for example, in home laundry and disinfecting for hospital laundry. The methods are similar to those described above. For example, the washings are soaked in an aqueous solution containing the water-soluble phthalocyanine compounds that were described in this invention under photo-irradiation. In addition, the phthalocyanine compounds can be used for disinfection of medical appliances and instruments, floors in hospitals, walls, and home furniture. In this case, one method is to coat the aqueous solutions of the phthalocyanine compounds that are described in this invention on a surface and the wet surfaces are photo-irradiated. As an alternative disinfecting method, the phthalocyanine compounds in this invention can be mixed with water of swimming pools or drained water from water purification systems to disinfect these waters under photo-irradiation. The following are detailed examples of this invention.

[0025]

[Execution Example 1]

(Execution Example 1) A 5 g piece of cotton cloth (e.g. a part of a dish towel) stained with tea was treated in 500 ml of an aqueous solution containing 0.01% of the type C compound with abbreviation ZnPcF12(PhO)4 (number of the sulfonation: 5) and 1% of a laundry detergent with stirring under irradiation by a 180 W infrared lamp. The cotton cloth was rinsed and dried. The stains on the cotton cloth completely disappeared, demonstrating this compound's bleaching effect.

[0026]

(Execution Examples 2~10) The bleaching effect was also examined in exactly the same manner as in example 1, but changing ZnPcF12(PhO)4 in example 1 with the compounds listed in Table 1. The experiments demonstrated that each compound listed in Table 1 has some disinfecting effect.

[0027]

(Execution Example 11) An aqueous solution which contains 0.1 ppm of the type A compound with abbreviation ZnPcF8(PhO)8 (number of sulfonation: 13) was prepared in a cooled beaker. A suspension of yellow staphylococcus (*Staphylococcus aureus*) IFO 12732 was added to the mixture. This suspension contained approximately 106/ml of staphylococcus and was irradiated by an infrared lamp located 15 cm above. Afterwards, the disinfecting effect was examined by checking the number of colonies using the usual agar culture method. As a result, it was observed that the number of staphylococcus decreased to approximately 50/ml, demonstrating this compounds disinfecting effect.

[0028]

(Execution Examples 12~22) The disinfecting effect was also examined in exactly the same manner as in example 11, but changing ZnPcF8(PhO)8 in example 11 with the compounds listed in Table 2. The yellow staphylococcus or coli bacillus (*Escherichia coli*) IFO 13500 were used with the compounds in Table 2. As a result, the experiments demonstrated that each compound in Table 2 has a disinfecting effect.

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[0029]

(Table 1)

| Execution Example | Donor Compound | | | | Bleaching Effect |
|-------------------|----------------|------------|-----------------|-------------------|------------------|
| | Structure No. | Core Metal | Sulfonic Number | Concentration (%) | |
| 2 | A-1 | Zn | 12 | 0.01 | ○ |
| 3 | A-9 | AlCl | 6 | 0.001 | △ |
| 4 | A-10 | Zn | 11 | 0.01 | ○ |
| 5 | A-15 | Zn | 5 | 0.01 | ○ |
| 6 | B-1 | CaCl | 13 | 0.01 | ○ |
| 7 | C-4 | Zn | 4 | 0.01 | ○ |
| 8 | C-6 | Zn | 5 | 0.01 | ○ |
| 9 | D-1 | Zn | 5 | 0.01 | ○ |
| 10 | D-9 | Zn | 2 | 0.01 | △ |

Bleaching effect confirmed: △

Bleaching effect confirmed but insufficient: ○

No Bleaching Effect: ×

[0030]

(Table 2)

| Execution Example | Donor Compound | | | | Type of Bacteria | Density of Bacteria after Sterilization (Unit/ml) |
|-------------------|----------------|------------|-----------------|-------------------|------------------|---|
| | Structure No. | Core Metal | Sulfonic Number | Concentration ppm | | |
| 12 | A-1 | Zn | 12 | 0.5 | B | 150 |
| 13 | A-9 | AlCl | 6 | 0.01 | B | 100 |
| 14 | A-14 | Zn | 7 | 0.1 | A | 50 |
| 15 | A-15 | Zn | 5 | 0.1 | A | 50 |
| 16 | B-1 | GaCl | 13 | 0.05 | A | 100 |
| 17 | C-1 | Zn | 5 | 0.1 | B | 100 |
| 18 | C-6 | Zn | 5 | 0.1 | A | 50 |
| 19 | D-1 | Zn | 4 | 0.01 | B | 150 |
| 20 | D-9 | Zn | 4 | 0.01 | A | 100 |

Type of Bacteria A: Staphylococcus Aureus
B: Escherichia Coll